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Results of Audit 6

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ANALYSIS OF EPA PROTOCOL GASES USED FOR CALIBRATION AND AUDITS OF CONTINUOUS EMISSION MONITORING SYSTEMS AND AMBIENT AIR ANALYZERS - RESULTS OF AUDIT 6

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16. ABSTRACT

A performance audit was conducted on EPA Protocol Gases used for calibration and audits of continuous emission monitoring systems and ambient air analyzers. Fifty gaseous pollutant calibraton standards were purchased from eleven specialty gas producers. These standards contained sulfur dioxide in nitrogen (70 and 300 ppm), nitric oxide in nitrogen (70 and 400 ppm), and carbon monoxide in air (30 ppm). Seventy percent of the producers' certified concentrations were accurate to within plus or minus 2 percent and 94 percent of the concentrations were accurate to within plus or minus 5 percent. These accuracies are significantly better than the accuracies obtained during a 1981 audit of commercial cylinder gases. In general, the lower concentration sulfur dioxide EPA Protocol Gases were less accurate than other EPA Protocol Gases. A secondary purpose of the audit was to examine the EPA Protocol Gases certificates of analysis for the inclusion of all data required by the protocol. In general, the producers supplied most of the information required on their certificates of analysis.

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ANALYSIS OF EPA PROTOCOL GASES USED FOR CALIBRATION AND AUDITS OF CONTINUOUS EMISSION MONITORING SYSTEMS AND AMBIENT AIR ANALYZERS - RESULTS OF AUDIT 6

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A performance audit was conducted on EPA Protocol Gases used for calibration and audits of continuous emission monitoring systems and ambient air analyzers. Fifty gaseous pollutant calibration standards were purchased from eleven specialty gas producers. These standards contained sulfur dioxide in nitrogen (70 and 300 ppm), nitric oxide in nitrogen (70 and 400 ppm), and carbon monoxide in air (30 ppm). Their pollutant concentrations were measured at RTI using source-level and ambient-level air pollution monitoring instruments. NBS Standard Reference Materials were used as the reference standards for the measurements. Confirmatory measurements of selected EPA Protocol Gases were performed at EPA's Standards Laboratory in Research Triangle Park. EPA's measurements were in good agreement with RTI's measurements. Seventy percent of the producers' certified concentrations were accurate to within plus or minus 2 percent and 94 percent of the concentrations were accurate to within plus or minus 5 percent. These accuracies are significantly better than the accuracies obtained during a 1981 audit of commercial cylinder gases. In general, the lower concentration sulfur dioxide EPA Protocol Gases were less accurate than other EPA Protocol Gases. A secondary purpose of the audit was to examine the EPA Protocol Gases' certificates of analysis for the inclusion of all data required by the protocol. In general, the producers supplied most of the information required on their certificates of analysis.

INTRODUCTION

Recently, the U.S. Environmental Protection Agency (EPA) published a proposed rule on quality assurance requirements for compliance of gas continuous emission monitoring systems (CEMS) (1). One part of these requirements is a quarterly assessment of data accuracy using a relative accuracy audit, a cylinder gas audit or an EPA-approved alternative. The proposed rule specifies that the audit cylinder gases be certified by comparison to National Bureau of Standards (NBS) Standard Reference Materials (SRMs) or NBS/EPA-approved gas manufacturer's Certified Reference Materials (CRMs) following EPA Traceability Protocol No. 1 (2). These gases are known as EPA Protocol Gases. The proposed rule makes the implicit assumption that the concentrations of the EPA Protocol Gases have been certified with sufficient accuracy such that the CEMS' accuracy can be established. This paper reports the results of a performance audit of EPA Protocol Gases. The purposes of the audit were (1) to document the accuracy of the certified concentrations of EPA Protocol Gases that were procured from commercial specialty gas producers and (2) to examine the producers' certificates of analysis for the inclusion of all data required by the protocol. Research Triangle Institute (RTI) performed the audit under contract to EPA. This audit was a follow-on to previous audits of commercial cylinder gases. Between 1978 and 1981, RTI conducted five audits of commercial cylinder gases at source concentrations. The results of these audits were reported at a 1981 APCA specialty conference on continuous emission monitoring (3). RTI has also conducted similar audits of NBS/EPA-approved CRMs which are prepared and analyzed by specialty gas producers (4).

AUDIT PROCEDURE

The first step in the audit was a telephone poll of specialty gas producers to determine whether they produced and sold EPA Protocol Gases. Eleven of the thirteen producers who were contacted responded that they sold EPA Protocol Gases. These eleven producers are listed in Table 1. RTI and an anonymous third party then purchased EPA Protocol Gases from all eleven producers. The third party was used to assure that the standards were of typical quality. The nominal concentrations and compositions of the standards that were purchased are given below:

- 70 parts per million (ppm) nitric oxide and less than 1 ppm nitrogen dioxide in nitrogen;
- 400 ppm nitric oxide in nitrogen·
- 70 ppm sulfur dioxide in nitrogen
- 300 ppm sulfur dioxide in nitrogen; and
- 30 ppm carbon monoxide in air.

The anonymous third party purchased the nitric oxide and sulfur dioxide EPA Protocol Gases and RTI purchased the carbon monoxide EPA Protocol Gases. The price of these standards ranged between $174 and $425 with the mean price being $281. Although the cylinder material was not specified when the EPA Protocol Gases were ordered, all the standards were delivered in aluminum cylinders. The higher concentration standards are typical of those which are used for calibrating and auditing stationary source CEMS. These standards were specified to be prepared and analyzed according to EPA Traceability Protocol No. 1. The lower concentration standards are typical of those which are used for calibrating and auditing ambient air quality analyzers. These standards were specified to be prepared and analyzed according to EPA Traceability

Protocol No. 2. This audit differs from the earlier audits of commercial cylinder gases because the purchase specifications for the earlier audits did not call for any particular preparatory or analytical protocol to be followed. Instead, the commercial cylinder gases were only specified to be analyzed and certified standards and none were certified as EPA Protocol Gases by their producers. As a result, the current audit can be used to determine whether EPA Protocol Gases are more accurate standards than more typical certified gas mixtures.

When the standards were delivered to RTI, their pollutant concentrations were measured according to the analytical procedures described in the next section. If the producer's certified concentrations differed from RTI's measured concentration by more than 3.0 percent, the standard was sent to EPA's Standards Laboratory (Quality Assurance Division, Environmental Monitoring Systems Laboratory) in Research Triangle Park. The standard was measured there with independent analytical instrumentation and different SRM reference standards to provide an independent and confirmatory analysis of the standard.

RTI ANALYTICAL PROCEDURES

Measurements of the EPA Protocol Gases were made using source-level or ambient-level air pollution monitoring instruments. The analytical principles used by the instruments are chemiluminescence for nitric oxide, ultraviolet fluorescence for sulfur dioxide, and non-dispersive infrared spectroscopy for carbon monoxide. The voltage output from the instruments was recorded on a strip chart recorder and an averaging data logger. The strip chart trace was checked to insure that a stable reading was being obtained for each cylinder measurement. Ten to twenty voltage readings were used for each mean voltage.

The procedure that was used for the analysis of the EPA Protocol Gases is a modification of the procedure that is used for performance audits of CRMs (4). The pollutant concentrations of the EPA Protocol Gases were determined by direct comparison with the two NBS SRMs whose concentrations bracket those of the standards. For example, 50 and 100 ppm NBS SRMs were the reference standards for the analysis of the 70 ppm EPA Protocol Gases. All gases were analyzed without dilution. A sampling manifold using solenoid valves and a digital timer allowed automated sequential measurements of the two reference standards and as many as six EPA Protocol Gases. All components of the sampling manifold in contact with the gas stream were made of stainless steel or Teflon. This eight-cylinder measurement cycle was repeated at least four times. The first measurement cycle was considered to be a purge cycle and was not included in any calculations. The measurement cycle approach allows the detection of short-term calibration drift because reference standard measurements precede and follow each EPA Protocol Gas measurement. The analyzer's calibration equation is recalculated for each EPA Protocol Gas measurement by linear interpolation between the two adjacent pairs of SRM measurements and thereby compensates for any drift. The sampling manifold pressure was constantly monitored to assure that the sample flowrate through the analyzer was the same for all the cylinders.

A mean measured concentration was calculated for each EPA Protocol Gas from the three or more measured concentrations. In general, the coefficient of variation for these measurements was less than 0.5 percent relative. An acceptance limit of one percent relative was established for the coefficient of variation. If this limit was exceeded, it was taken as a sign of a lack of stabilization or of noise problems and the measurements were repeated.

In addition to the two SRMs that were used as reference standards for the EPA Protocol Gas measurements, other SRMs were measured to establish the linearity of each analyzer's calibration curve. A slight non-linearity was discovered for the 300 ppm sulfur dioxide measurements and a quadratic correction equation was used to compensate for this non-linearity.

EPA regulations for ambient air quality monitoring (5) specify that the nitric oxide standard contain 50 to 100 ppm nitric oxide in nitrogen with less than 1 ppm nitrogen dioxide. During the audit, the nitrogen dioxide concentration in the 70 ppm nitric oxide in nitrogen EPA Protocol Gases was calculated. Following measurement of the nitric oxide concentrations, the instrument was switched to its nitrogen oxides mode and a single nitrogen oxides measurement for each cylinder was made. The nitrogen dioxide concentration was obtained by subtracting the mean nitric oxide concentration from the nitrogen oxides concentration.

AUDIT RESULTS FOR EPA PROTOCOL GAS ACCURACY

The results of the audit of the EPA Protocol Gases are summarized in Tables 2 through 4 in which the producers' certified concentrations and RTI's measured concentrations for these cylinders are listed. The accuracy of the certified concentrations is defined as the percent difference between the certified and the measured concentrations. It should be noted that one standard was found to be empty at the start of the audit. Three standards from one producer and one standard from another producer had to be returned for a second analysis as required by EPA Protocol No. 1 after it was determined that each standard had been analyzed only one time.

Confirmatory analyses were performed at EPA's Standard Laboratory for those EPA Protocol Gases in which the percent difference was not within $\pm$ 3.0 percent. The results of EPA's analyses are presented in Table 5. The percent differences between the producer's certified and EPA's measured concentrations are listed. EPA's measured concentrations are in good agreement with the corresponding RTI measurements which are also shown in Table 5. Eight of the eleven pairs of RTI/EPA values are within 1.2 percent of each other. This level of agreement supports the belief that RTI correctly determined the accuracy of the EPA Protocol Gases' certified concentrations.

The calculated nitrogen dioxide concentrations of the 70 ppm nitric oxide in nitrogen EPA Protocol Gases are generally less than 1 ppm. However, these values were more uncertain than the nitric oxides measurements because they were calculated by subtracting two large numbers and because there was only a single nitrogen oxides measurement. Nevertheless, two of the EPA Protocol Gases had calculated nitrogen dioxide concentrations of 1.3 and 1.5 ppm. These concentrations were found to be significantly different from zero using a statistical test for outlier data.

The accuracy of EPA Protocol Gases as a class can be assessed by the frequency distributions given in Table 6. Seventy percent of the producers' certified concentrations were accurate within 2 percent, and 94 percent of the concentrations were accurate to within 5 percent. The 70 ppm sulfur dioxide standards, as a group, were less accurate than the other standards. Thirty-three percent of this group were accurate to within 2 percent and 77 percent of the group were accurate to within 5 percent.

The data in Table 6 can be compared with the corresponding data from the 1981 audit of commercial cylinder gases (6) which is given in Table 7. The 1981 audit is typical of the five commercial cylinder gas audits that were conducted. The commercial cylinder gases exhibit significantly greater percent differences than do the EPA Protocol Gases. Forty-five percent of the of the producers' certified concentrations were accurate to within 2 percent. and 65 percent of the concentrations were accurate to within 5 percent. It should be again noted that the commercial cylinder gases were ordered without specification of any particular analytical protocol.

INFORMATION CONTAINED ON CERTIFICATES OF ANALYSIS

The second purpose of the audit was to investigate the completeness of the information contained on the producers' certificates of analysis for the EPA Protocol Gases. The protocol specifies that a written analysis report should be prepared which certifies that the cylinder gas has been analyzed according to the protocol. In addition, the analysis report should contain:

1. Cylinder number;
2. Mean concentration of cylinder gas on last analysis date;
3. Replicate analysis data;
4. Balance gas used;
5. NBS SRM numbers used as primary standards; and
6. Analytical principle used; and
7. Last analysis date.

A summary of the information which was contained on the certificates is given in Table 8. In several cases, RTI had to request that the producer send the certificate of analysis because none had been delivered with the EPA Protocol Gas or within a reasonable period afterwards. In addition, several certificates did not explicitly state that the cylinder gas had been analyzed according to the protocol. The data most frequently omitted from the certificates were the replicate analysis data and the last analysis date.

CONCLUSIONS.

The audit of EPA Protocol Gases found that 70 percent of the producer's certified concentrations were accurate to within plus or minus 2 percent and that 94 percent of the concentrations were accurate to within plus or minus 5 percent. These accuracies are significantly better than the accuracies that were found during a 1981 audit of commercial cylinder gases. In the earlier audit, 45 percent of the certified concentrations were accurate to within plus or minus 2 percent and 65 percent of the concentrations were accurate to within plus or minus 5 percent. These data suggest that more accurate calibration standards can be obtained by ordering EPA Protocol Gases than by ordering commercial cylinder gases for which no rigorous analytical protocol is specified. However, improvements of analytical capability within the specialty gas industry between 1981 and 1985 may also be a factor in the improved accuracy. Additionally, purchasers of lower concentration sulfur dioxide in nitrogen EPA Protocol Gases should be aware that these standards, as a group, may be less accurate than other EPA Protocol Gases.

In general, the producers supplied most of the information required on their certificates of analysis. However, improvements are needed in the reporting of replicate analysis data and the date of the last analysis.

FUTURE PLANS

EPA plans to conduct additional audits of EPA Protocol Gases in the future. These audits will allow EPA to assess continually the accuracy of cylinder gases that are prepared and analyzed by specialty gas producers according to EPA Traceability Protocol Nos. 1 and 2.

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Table 1. Specialty Gas Products Included in Audit of EPA Protocol Gases

Specialty Gas Producer	Production Facility
Airco Industrial Gases	Research Triangle Park, North Carolina
Air Products and Chemicals (1)	Tamaqua, Pennsylvania
Big Three Industries	La Porte, Texas
Liquid Carbonic	Harrison, New Jersey
Matheson Gas Products (2)	East Rutherford, New Jersey
MG Industries	North Branch, New Jersey
National Specialty Gases	Research Triangle Park, North Carolina
Scientific Gas Products	South Plainfield, New Jersey
Scott-Marrin	Riverside, California
Scott Specialty Gases	Plumsteadville, Pennsylvania
Union Carbide, Linde Division	East Chicago, Indiana

(1) Air Products prepares and sells nitric oxide in nitrogen and sulfur dioxide in nitrogen EPA Protocol Gases, but not carbon monoxide in air EPA Protocol Gases.

(2) Matheson prepares and sells nitric oxide in nitrogen EPA Protocol Gases, but not sulfur dioxide in nitrogen or carbon monoxide in air EPA Protocol Gases.

Table 2. Summary of Results From the Audit of Sulfur Dioxide In Nitrogen EPA Protocol Gases

	Nominal 70 ppm Sulfur Dioxide			Nominal 300 ppm Sulfur Dioxide		
Producer	Producer Certified $[SO_2]$ (ppm)	RTI Measured $[SO_2]$ (ppm)	Percent Difference (1)	Producer Certified $[SO_2]$ (ppm)	RTI Measured $[SO_2]$ (ppm)	Percent Difference (1)
Airco	71.6	72.6	-1.3	299.	304.9	-1.9
Air Products	67.4	61.4	9.8	294.	296.3	-0.8
Big Three	72.3	74.3	-2.8	316.	324.8	-2.7
Liquid Carbonic	68.	66.7	2.0	291.	296.6	-1.9
MG Industries	80.7	83.3	-3.1	320.	317.5	0.8
National Spec.	73.2	71.0	3.2	306. (2)	300.3	1.9
Sci. Gas Prod.	66.	70.9	-7.0	302.	250.9	20.4
Scott-Marrin	69.7	70.5	-1.1	296.1	297.1	-0.3
Scott Spec.	81.86	85.0	-3.6	318.1	319.1	-0.3
Union Carbide	74.	--- (3)	---	318.	315.8	-0.7

(1) Percent Difference = $100 \left| \frac{\text{Certified } [SO_2] - \text{Measured } [SO_2]}{\text{Measured } [SO_2]} \right|$

(2) This cylinder originally was not analyzed by EPA Protocol and had to be returned to the producer for EPA Protocol analysis.

(3) Cylinder found to be empty at the start of the audit.

Table 3. Summary of Results From the Audit of Nitric Oxide In Nitrogen EPA Protocol Gases

	Nominal 70 ppm Nitric Oxide			Nominal 400 ppm Nitric Oxide		
Producer	Producer Certified [NO] (ppm)	RTI Measured [NO] (ppm)	Percent Difference (1)	Producer Certified [NO] (ppm)	RTI Measured [NO] (ppm)	Percent Difference (1)
Airco	65.7	67.9	-3.2	389.	386.9	0.6
Air Products	70.0	68.4	2.3	400.0	406.5	-1.6
Big Three	70.9	68.0	4.3	439.6	443.7	-0.9
Liquid Carbonic	70.8	70.3	0.7	392.	400.5	-2.1
Matheson	70.	67.2	4.2	400.	390.9	2.3
MG Industries	74.5	74.0	0.6	408.	407.9	0.0
National Spec.	70.2 (2)	69.4	1.1	404.5 (2)	400.9	0.9
Sci. Gas Prod.	74.	74.1	-0.2	432.	429.5	0.6
Scott-Marrin	70.4	70.5	-0.2	402.6	401.4	0.3
Scott Spec.	73.22	71.8	0.2	408.6	411.5	-0.7
Union Carbide	69.0	69.2	-0.3	407.	408.8	-0.4

(1) Percent Difference = $100 \left[\frac{\text{Certified [NO]} - \text{Measured [NO]}}{\text{Measured [NO]}} \right]$

(2) This cylinder originally was not analyzed by EPA Protocol and had to be returned to the producer for EPA Protocol analysis.

Table 4. Summary of Results From the Audit of Carbon Monoxide In Air EPA Protocol Gases

	Nominal 30 ppm Carbon Monoxide		
Producer	Producer Certified [CO] (ppm)	RTI Measured [CO] (ppm)	Percent Difference (1)
Airco	31.9 (2)	31.83	0.2
Big Three	30.5	29.76	2.5
Liquid Carbonic	31.	31.11	-0.3
MG Industries	28.9	28.81	0.3
National Spec.	30.65	30.44	0.7
Sci. Gas Prod.	29.3	29.38	-0.3
Scott-Marrin	29.3	29.49	-0.6
Scott Spec.	30.94	30.82	0.4
Union Carbide	29.4	29.88	-1.6

(1) Percent Difference = $100 \left[\frac{\text{Certified [CO]} - \text{Measured [CO]}}{\text{Measured [CO]}} \right]$

(2) This cylinder originally was not analyzed by EPA Protocol and had to be returned to the producer for EPA Protocol analysis.

Table 5. Summary of Results From EPA Standards Laboratory's Confirmatory Analysis of EPA Protocol Gases (1)

Producer	Nominal Contents	EPA Protocol Gas Concentrations			Percent Difference (2)	
		Producer Certified (ppm)	RTI Measured (ppm)	EPA Measured (ppm)	Producer-to-EPA	RTI-to-EPA
Airco	70 ppm NO	65.7	67.9	68.3	-3.8	-0.6
Big Three	70 ppm NO	70.9	68.0	68.5	3.5	-0.7
Matheson	70 ppm NO	70.	67.2	67.5	3.7	-0.4
Air Products	70 ppm SO_2	67.4	61.4	60.7	11.0	1.2
MG Industries	70 ppm SO_2	80.7	83.3	83.0	-2.8	0.4
National Spec.	70 ppm SO_2	73.2	71.0	70.5	3.9	0.7
Sci. Gas Prod.	70 ppm SO_2	66.	70.9	70.9	-6.9	0.0
Scott Spec.	70 ppm SO_2	81.86	85.0	84.9	-3.6	0.1
Big Three	300 ppm SO_2	316.	324.8	335.	-5.7	-3.0
MG Industries (3)	300 ppm SO_2	320.	317.5	324.	-1 2	-2.0
Sci. Gas Prod.	300 ppm SO_2	302.	250.9	258.	17.0	-2.8

(1) Confirmatory analyses were performed at EPA's Standards Laboratory for those EPA Protocol Gases in which the producer's certified concentration and RTI's measured concentration differed by more than 3.0 percent.

(2) Percent Difference = $100 \left[\frac{\text{Producer Conc.} - \text{EPA Conc.}}{\text{EPA Conc.}} \right]$ or $100 \left[\frac{\text{RTI Conc.} - \text{EPA Conc.}}{\text{EPA Conc.}} \right]$

(3) This standard was analyzed at EPA even though the producer's certified concentration and RTI's measured concentration differed by only 0.8 percent.

Table 6. Frequency Distribution for Difference Between Producer Certified and RTI Measured Concentrations from Audit of EPA Protocol Gases (Audit No. 6)

Protocol Gas Composition	Nominal Concentration (ppm)	Absolute Value of Percent Difference (1)			
		0 to 2	2 to 5	5 to 10	>10
SO_2/N_2	70	3 (2)	4	2	0
	300	8	1	0	1 (3)
NO/N_2	70	7	4	0	0
	400	9	2	0	0
CO/Air	30	8	1	0	0
	Total	35	12	2	1

(1) Percent Difference = $100 \left| \frac{\text{Certified Conc.} - \text{Measured Conc.}}{\text{Measured Conc.}} \right|$

(2) This is the number of cylinders whose accuracies fall in this range.

(3) This value is 20.4 percent.

Table 7. Frequency Distribution for Difference Between Producer Certified and RTI Measured Concentrations from 1981 Audit of Commercial Cylinder Gases (Audit No. 5)

Cylinder Gas Composition	Nominal Concentration (ppm)	Absolute Value of Percent Difference (1)			
		0 to 2	2 to 5	5 to 10	>10
SO_2/N_2	90	2 (2)	2	3	6 (3)
	500	3	2	5	3
NO/N_2	50	5	5	2	2
	300	11	2	1	0
CO/N_2	50	7	2	3	2
	500	9	3	0	2
	Total	37	16	14	15

(1) Percent Difference = $100 \left| \frac{\text{Certified Conc.} - \text{Measured Conc.}}{\text{Measured Conc.}} \right|$

(2) This is the number of cylinders whose accuracies fall in this range

(3) These values are 11.8, 12.1, 31.7, 38.4, 40.5, and 112. percent.

Table 8. Summary of Information Reported on Certificates of Analysis for EPA Protocol Gases

Producer	Certs. Rec'd	Protocol Listed on Cert.	Cyl. No.	Mean Conc.	Replic. Anal. Data	Bal. Gas	NBS SRM No.	Anal. Meth. Used	Last Anal. Date
Airco (1)	Y	Y (2)	Y	Y	N	Y	N (3)	Y	N
Air Products	Y (4)	Y	Y	Y	Y	Y	Y	Y	Y
Big Three	Y	N	Y	Y	N	Y	Y	N	N
Liq. Carbonic	Y	N (4)	Y	Y	N	Y	Y (4)	Y (6)	N
Matheson	Y	Y	Y	Y	Y (5)	Y	Y	Y	Y
MG Industries	Y	Y	Y	Y	Y	Y	Y	Y	Y
Nat. Spec. (7)	Y	Y	Y	N	Y	Y	Y	Y	N (8)
Sci. Gas Prod.	Y	Y	Y	Y	N	Y	Y	Y	Y
Scott-Marrin	Y	Y	Y	Y	Y	Y	Y	Y	Y
Scott Spec.	Y	Y	Y	Y	Y	Y	Y	Y	Y
Union Carbide	Y (4)	Y	Y	Y	Y (9)	Y	Y	Y	Y

Y = Yes, N = No

(1) One cylinder originally was not analyzed according to EPA Protocol and had to be returned to the producer for EPA Protocol analysis.

(2) Some of the certificates did not designate the cylinder as an EPA Protocol Gas.

(3) The SRM's stamped cylinder number was listed instead of the SRM number.

(4) RTI had to request that the producer send this information for some or all the cylinders.

(5) Data are questionable because all six concentrations on each certificate are identical.

(6) This certificate stated that carbon monoxide was analyzed by a "specific carbon monoxide analyzer" but did not state the analytical principle used.

(7) Three cylinders originally were not analyzed according the EPA Protocol and had to be returned to the producer for EPA Protocol analysis.

(8) The expiration data was listed instead of the last analysis date.

(9) Replicate data from only one analysis was reported on the certificate.